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(54) Title: POLYAMIDE-CONTAINING LIGANDS COVALENTLY BONDED TO SUPPORTS, POLYAMIDE-CONTAINING RESINS, AND METHODS FOR REMOVING METALS FROM SOLUTIONS

(57) Abstract: Compositions and methods for selectively binding metal ions from source solutions are disclosed. The compositions include 1) polyamide-containing ligands covalently bonded to a particulate solid support, and 2) polyamide-containing polymeric resins. In the case of the ligand bonded to the solid support, the ligand is bonded or tethered to the solid support through a hydrophilic spacer such that the overall formula is SS-A-X-L. In this formula, SS is a particulate solid support such as silica or a polymeric bead, A is a covalent linkage mechanism, X is a hydrophilic spacer grouping, and L is a polyamide-containing ligand having three or more amide groups and two or more amine nitrogens separated by at least two carbons with the proviso that when SS is a particulate organic polymer, A-X may be combined as a single covalent linkage. With respect to the polyamide ligand-containing polymeric resin, this composition is a reaction product of a hydroxymethylated polyamide ligand and a polymerization and/or crosslinking agent.

## POLYAMIDE-CONTAINING LIGANDS COVALENTLY BONDED TO SUPPORTS, POLYAMIDE-CONTAINING RESINS, AND METHODS FOR REMOVING METALS FROM SOLUTIONS

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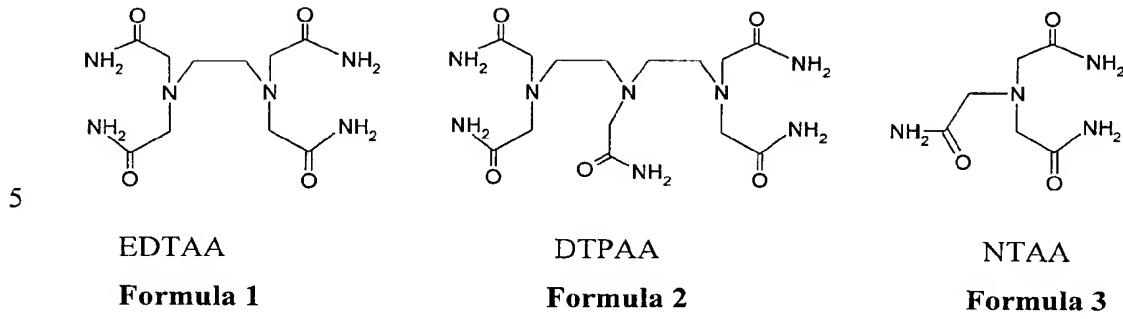
FIELD OF THE INVENTION

The present invention relates to polyamide-containing ligands covalently bonded to inorganic and organic solid supports and polyamide-containing polymeric resins. Methods of using such compositions for removing, separating and concentrating certain desired metal ions from solutions are also disclosed, even when the desired ions are in the presence of other metal ions and/or hydrogen ions at much higher concentrations.

15 BACKGROUND OF THE INVENTION

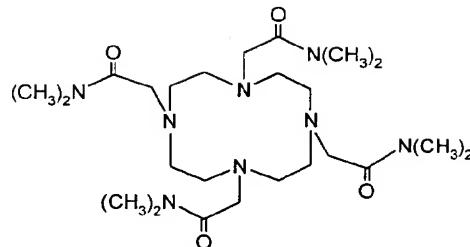
Effective methods for the separation and recovery of particular ions such as the transition, post-transition and alkaline earth metal ions from solution mixtures containing these and other metal ions are of great importance in modern technology. Particularly, it is difficult to separate and recover certain metal ions such as Cd<sup>2+</sup>, Pb<sup>2+</sup>, Ag<sup>+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Sr<sup>2+</sup>, and/or Ca<sup>2+</sup> from the presence of even moderate amounts of hydrogen ion (H<sup>+</sup>). It is also very difficult to remove the mentioned desired metal ions when present at low concentrations in solutions that contain other, non-desirable metal ions at much greater concentrations. Thus, there is a real need for a composition of matter and an associated method that may be used for selectively separating certain transition, post-transition, and alkaline earth metal ions from other non-desirable ions.

25 It is known that ethylenediaminetetraacetamide (EDTAA), diethylenetriaminepentaacetamide (DTPAA), and nitrilotriacetamide (NTAA) form strong complexes with various metal ions in solution. These molecules may 30 be shown as Formulas 1 – 3 respectively below:

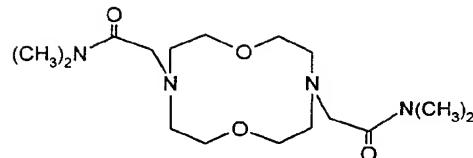


10 J.M. Grana-Molares, C. Baluja-Santos, A. Alvarez-Devesa and F. Bermejo-Martinez, Etude Spectrophotometrique des Complexes du Cobalt(III) avec les Amides de l'EDTA et du DTPA, Analysis, Volume 7, 249-252 (1979) (report on the synthesis of EDTAA and DTPAA and their ability to complex Co(III) as shown by a spectrophotometric technique). In a different study, L. Przyborowski  
15 showed that NTAA and EDTAA could be prepared by modifying known methods and that Cu(II) formed strong complexes with NTAA. L. Przyborowski, Complex Compounds of Amides and Thioamides of Aminopolycarboxylic Acids, Part III. Synthesis, Properties and Copper(II) Complexes of Nitrilotriacetotriamide and Ethylenediaminetetraacetotetraamide, Roczniki  
20 Chemii, Volume 44, 1883-1893 (1970).

More recently, a great deal of research has been done in the synthesis and metal ion complexation properties of polyamide-containing azacrown ethers such as those containing acetamide, propionamide, and peptide side arms. R. Kataky, K.E. Matthes, P.E. Nicholson, D. Parker and H-J. Buschmann, Synthesis and Binding Properties of Amide-Functionalized Polyazamacrocycles, Journal of the Chemical Society, Perkin Transactions 2, 1425-1432 (1990) (reported on the synthesis and complexation properties of per-N-(dimethylacetamido)- substituted triaza-9-crown-3, aza-12-crown-4, diaza-12-crown-4, and tetraaza-12-crown-4). The ligating agents 1,4,7,10-tetrakis(N,N-dimethylacetamido)-1,4,7,10-  
25 tetraazacyclododecane and 1,7-dioxo-4,10-bis(N,N-dimethylacetamido)-4,10- diazacyclododecane are two chemical structures that were synthesized and which  
30 are representative of polyamide-containing ligating agents of the present invention. These ligating agents are shown respectively below in Formulas 4 and 5:



Tetraazacyclododecane

**Formula 4**

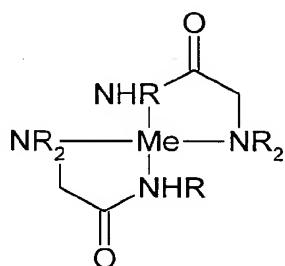
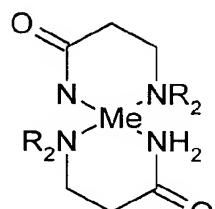
Diazacyclododecane

**Formula 5**

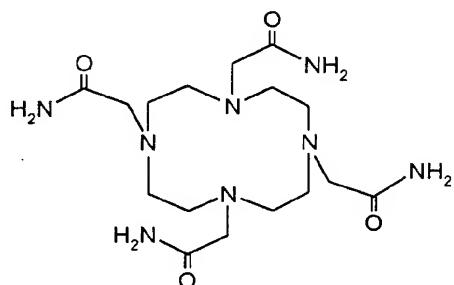
5 The diamide of Formula 5 was shown to form complexes with all of the alkali metal and alkaline earth metal cations. Further, this diamide was shown to have significant selectivity for  $\text{Ca}^{2+}$  over the other cations studied. However, a diamide similar to that of Formula 5, but containing one more methylene group in each amide-containing arm (thus, having two N,N-dimethylpropioamido substituents), was shown to form weaker complexes with these same metal ions.

10 Further studies of amide ligands such as those depicted by formulas 4 and 5 have concluded that the size of the metal ion-ligand chelate ring determines the strength of the interaction between the ligand and the metal ions. For example, a five-membered ring favored the smaller cations over a six-membered ring.

15 Representative of fully chelated metals (Me) having five- and six-membered amide rings attached are shown in Formulas 6 and 7 respectively below:

**Formula 6****Formula 7**

Wainwright, The Amide Oxygen as a Donor Group. Metal Ion Complexing Properties of Tetra-N-Acetamide Substituted Cyclen: A Crystallographic, NMR, Molecular Mechanics and Thermodynamic Study, Journal of the American Chemical Society, Volume 117, 6698-6707 (1995). Further, in this article, the authors reported the synthesis of 1,4,7,10-tetraazacyclododecane (DOTAM) which is the unsubstituted amide analogue of the tetraamide of Formula 4. DOTAM is capable of forming complexes with a host of metal ions including many transition and post-transition metal ions. DOTAM also forms strong complexes with  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , even at pH levels as low as 0.3 which is



10 equivalent to a hydrogen ion concentration of 0.5 Molar. DOTAM may be represented by Formula 8 below:

DOTAM

Formula 8

15

The articles cited above disclose procedures for synthesizing and demonstrating limited useful complexation properties of polyamide-containing ligand molecules. However, researchers have not previously been able to incorporate polyamide-containing ligands into solid phase separation systems. 20 This is significant because these polyamide-containing ligands merely act as a solute in solution by complexing with selected ions, but provide no effective means for ion separation.

25 The use of polymeric resins *per se* for selective removal of ions is not a new concept of itself. In U.S. Patent No. 5,656,702, the use of poly(hydroxyarylene) polymeric resins is disclosed for removing alkali metals, particularly cesium, from industrial streams. Additionally, the use of ligands bonded to solid supports is also not a new concept. Various ligands have been

bonded to solid supports for both chromatographic and non-chromatographic separation systems. However, never before have polyamide ligand-containing polymeric resins or polyamide ligand ligands bonded to solid supports been successfully synthesized that can be used in a solid phase separation system to 5 concentrate and remove desired metal ions such as members selected from the group consisting of Cd<sup>2+</sup>, Pb<sup>2+</sup>, Ag<sup>+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Sr<sup>2+</sup>, and/or Ca<sup>2+</sup> from source solutions. Therefore, it would be useful to provide such compositions and associated methods for separating these and other desired metal ions.

10 SUMMARY OF THE INVENTION

The present invention is drawn to novel porous and/or non-porous particulate organic and/or inorganic solid supports covalently bonded to polyamide-containing ligands. When an inorganic solid support is used, the solid support is bonded to the polyamide-containing ligand through a covalent linkage 15 mechanism and a hydrophilic spacer grouping. When the particulate solid support is an organic resin or polymer, such as a polyacrylate bead, the polyamide-containing ligand may be bonded directly to an activated polar group on the polymer through a covalent linkage mechanism. A unique composition of matter of this invention comprises polyamide-containing ligands having three or 20 more amide groups (NHC(O)CH<sub>2</sub>), two or more amine nitrogens separated by at least two carbons and at least one solid support linkage.

The present invention is also drawn to polyamide ligand-containing polymeric resins for removing, separating, and/or concentrating certain desired divalent metal ions including transition, post-transition, and alkaline earth metal ions from source solutions. The unique composition of matter of this invention is 25 a polyamide ligand-containing polymeric resin which has been polymerized and/or crosslinked. These resins are generally a reaction product of a hydroxymethylated polyamide ligand and a polymerization and/or crosslinking agent. Specifically, the polymeric resins of the present invention are comprised 30 of from 10 to 50,000 polyamide ligand units wherein each polyamide ligand unit is defined by three or more amide groups, preferably from three to eight amide groups, and two or more amine nitrogen donor atoms separated by at least two carbons.

The invention is also drawn to the concentration and removal of certain

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desired divalent metal ions including transition, post-transition, and alkaline earth metal ions. The present invention is particularly useful for removing such ions as Cd<sup>2+</sup>, Pb<sup>2+</sup>, Ag<sup>+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Sr<sup>2+</sup>, and/or Ca<sup>2+</sup> from source solutions. This is true whether the desired ions are present at very low or very high 5 concentrations, i.e., from ppb to g/l.

The concentration of desired ions is accomplished by forming a complex of desired ions with a polyamide-containing ligand covalently bound to a solid support material or a polyamide-containing polymeric resin by flowing a source solution containing the desired ions through a column packed with polyamide-containing ligand bound solid support material or through a column packed with polyamide-containing polymeric resin material. This process enables the desired ions to complex with the polyamide-containing ligand portion of either 10 composition type disclosed herein. The metal ion and the polyamide-containing ligand are then decoupled by flowing a receiving liquid through the column (in much smaller volume than the volume of source solution passed through the 15 column) to remove and concentrate the desired ions in the receiving liquid solution. The receiving liquid or recovery solution forms a stronger complex with the desired ions than does the polyamide-containing ligand, or alternatively, temporarily forms a stronger interaction with the polyamide-containing ligand than does the desired metal ions. In either case, the desired metal ions are 20 quantitatively stripped from the ligand in a concentrated form in the receiving solution. The recovery of desired ions from the receiving liquid may be accomplished by various methods commonly known in the art including evaporation, electrowinning, and precipitation among others.

25

#### DETAILED DESCRIPTION OF THE INVENTION

A composition of the present invention comprises polyamide-containing ligands that are covalently bonded to an inorganic or organic solid support through a spacer and are represented by Formula 9 as follows:

30

SS-A-X-L

**Formula 9**

wherein SS is a solid support, A is a covalent linkage mechanism, X is a

hydrophilic spacer grouping, and L is a polyamide-containing ligand.

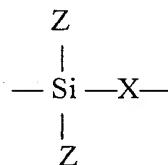
The SS-A-X- portion of Formula 9 is well known for use with ion binding ligands. Preferably, the solid support (SS) is an inorganic and/or organic particulate support material selected from the group consisting of silica, silica gel, silicates, zirconia, titania, alumina, nickel oxide, glass beads, phenolic resins, polystyrenes, and polyacrylates. However, other organic resins or any other hydrophilic organic and/or inorganic support materials meeting the above criteria can also be used.

The use of organic ion binding ligands attached to an SS-A-X- solid support by means of a covalent linkage spacer grouping is illustrated in U.S. Patents 4,943,375; 4,952,321; 4,959,153; 4,960,882; 5,039,419; 5,071,819; 5,078,978; 5,084,430; 5,173,470; 5,179,213; 5,182,251; 5,190,661; 5,244,856; 5,273,660; and 5,393,892. These patents, which disclose various spacers that can be used in forming an organic ligand attached to a solid support, are incorporated herein by reference.

When the solid support (SS) is an inorganic material such as silica, silica gel, silicates, zirconia, titania, alumina, nickel oxide, or glass beads, the covalent linkage (A) is a silane such that A-X may be represented by Formula 10 as follows:

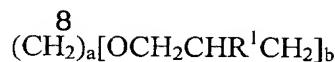
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**Formula 10**

where each Z is independently selected from the group consisting of Cl, Br, I, lower alkyl, lower alkoxy, substituted lower alkyl or substituted lower alkoxy and S (as used herein, lower alkyl or lower alkoxy means a group having 1 to 8 carbon atoms); and X is a spacer grouping represented by Formula 11 as follows:



**Formula 11**

wherein R<sup>1</sup> is a member selected from the group consisting of H, SH, OH, lower alkyl, and aryl; a is an integer from 2 to about 10; and b is 0 or 1. In Formula 11, the terminal carbon (or -CH<sub>2</sub>- group most distal to the solid support) may attach to the polyamide-containing ligand by any suitable bond. However, it is preferred that the terminal carbon on the spacer be covalently bonded to a nitrogen or another carbon present on the ligand.

Often, the terminal carbon on the spacer (X) will bond to either the carbon or the nitrogen found on an amide group of the polyamide-containing ligand. For example, if the ligand has 4 amide groups, one may be used to attach the ligand to the spacer (X) leaving 3 amide groups available for complexing desired ions. If the terminal carbon on the spacer (X) is to bond to an amide group of the ligand (L), Formula 12 below is representative of such an amide group:



**Formula 12**

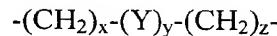
where m is 0 or 1; and n is 0 or 1 with the proviso that when m is 1, n is 0 and when m is 0, n is 1. Thus, the terminal carbon can either covalently bond to a nitrogen or a carbon atom of the amide group.

Conversely, the spacer (X) does not have to bond to an amide group at all. In some embodiments, the spacer (X) bonds directly to a nitrogen or carbon atom or other appropriate atom that is not part of an amide group. In other embodiments, the SS-A-X- portion will attach to the polyamide-containing ligand by replacing one of the amide groups. Therefore, the attachment of the spacer (X) to the polyamide-containing ligand (L) should be limited only by functionality.

When the particulate solid support (SS) is an organic resin or polymer, such as phenolic resins, polystyrenes, and polyacrylates, it will generally be a hydrophilic polymer or polymer derivatized to have a hydrophilic surface and contain polar functional groups. The polyamide-containing ligand (L) will then generally contain a functional grouping reactive with an activated polar group on

the polymer. The covalent linkage (A) and the spacer (X) will then be integrated, and may actually be a single linkage, formed by the reaction between the activated polar group from the polymer and the functional group from the ligand and may be represented by Formula 13 below:

5



**Formula 13**

10 where x is 0 or 1; y and z are independently 0 or an integer from 1 to 10; and Y is a functional group or aromatic linkage such as an ether (O), sulfide (S), imine (C=N), carbonyl (CO), ester (COO), thioester (CSO), amide (CONH), thioamide (CSNH), amine (NH), lower alkylamine (NR), sulfoxide (SO), sulfone (SO<sub>2</sub>), sulfonamide (SO<sub>2</sub>NH), phenyl (C<sub>6</sub>H<sub>5</sub>), benzyl (CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), and the like. At least one of x, y or z must be 1.

15 The polyamide-containing ligand (L) of the present invention is meant to include any ligand having three or more functional amide groups (NHC(O)CH<sub>2</sub>) capable of complexing with the desired metal ions and two or more amine nitrogens separated by at least two carbons. Representative examples of polyamide-containing ligands that have at least three amide groups and two or more amine nitrogens separated by at least two carbons include: ethylene bis(oxyethylenenitrilo)tetraacetic acid (EGTAM), diaza-18-crown-6-tetraamide, 20 ethylenediaminetetraacetamide-N-methylenepropanetetraamine (EDTAAMT), tris(2-aminoethyl)amine pentaamide (TREN PAM), and diethylenetriaminepentaacetamide (DTPAM). This list is intended only to be 25 representative of the possible ligands that may be used, the limiting factor being the presence of at least three amide groups and at least two amine nitrogens separated by two or more carbons. Further variations of these ligands may also be used. For example, tris(2-aminoethyl)amine pentaamide (TREN PAM) may be 30 alkyl or aryl substituted as illustrated in Examples 4B (dimethyl substituted) and 4C (phenyl substituted) respectively.

It is to be emphasized that the present invention does not reside in the discovery of the SS-A-X- portion of Formula 9. Rather, it is the discovery that the ion-binding and separation capabilities of the polyamide-containing ligand, when attached to an SS-A-X based solid substrates, are optimized. As

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summarized above, the present invention is drawn to a novel composition of matter comprising polyamide-containing ligand molecules covalently bound to solid support materials to form the compounds of Formula 9. However, the invention is also drawn to alternative compositions as described below.

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In an alternative embodiment, the polyamide ligand-containing polymeric resins of the present invention are a reaction product of a polyamide ligand and formaldehyde or other suitable compound capable of forming a hydroxymethylated polyamide ligand. The hydroxymethylated polyamide ligand is then polymerized using a polymerization and/or crosslinking agent to form the 10 polyamide ligand-containing polymeric resins. The polyamide ligand-containing polymeric resins of the present invention are comprised of from 10 to 50,000 polyamide ligand units wherein each polyamide ligand unit or monomer is defined by three or more amide groups, preferably from three to eight amide groups, as well as two or more amine nitrogen donor atoms separated by at least 15 two carbons. Each amide group of the polyamide ligand unit, after hydroxymethylation, may remain hydroxymethylated or be polymerized and/or crosslinked to other polyamide ligand units through a polymerization agent or a crosslinking agent. At least one of the amide groups of the resin must be polymerized or crosslinked, preferably from two to eight.

20

The structure of the present invention may be represented generally by Formula 14 as follows:



**Formula 14**

25

wherein L represents the polyamide-containing ligand having three or more amide groups, preferably from three to eight amide groups, and two or more amine nitrogens separated by at least two carbons, n may be an integer from about 10 to 50,000, m is at least three, preferably from three to eight, and X may 30 be CH<sub>2</sub>OH, CH<sub>2</sub>O-, CH<sub>2</sub>-, a crosslinking agent, or a resulting group from polymerization with the proviso that each X group is bonded individually to L and at least one X group per polyamide ligand unit is involved in the polymerization or crosslinking.

## 11

Amide groups of the ligand which remain hydroxymethylated after polymerization are free to bind with the desired metal ions according to the present invention. However, the amide groups of the ligand which are involved in the polymerization reaction or crosslinking may also be involved in the binding of the desired metal ions. In other words, it is not the purpose of the invention to describe specifically how each of the polymeric resins complex with each specific desired ion, only that the polymeric resins described herein will bind with the desired ions in various separation systems including non-chromatographic separation systems.

It is to be noted that the crosslinking agents or polymerization agents that may be used and the processes of crosslinking and/or polymerization are known in the art. For example, phenols, resorcinol, fluoroglucinol, aromatic or aliphatic amines, pyrroles, indoles, nitrates, esters, ketones, and nitriles, and/or other known crosslinking agents may be used. Further, polymerization agents that may be used include bisaldehydes, polyaldehydes, dihalogens, polyhalogens, dihalogens of diacids, polyhalogens of polyacids, diesters, polyesters, anhydrides of acids, diepoxides, polyepoxides, and/or other known polymerization agents.

In one preferred embodiment, a hydroxymethylated polyamide ligand may be polymerized linearly using a polymerization agent. In a second preferred embodiment, the generally linear polymer described above may be crosslinked using a crosslinking agent. In another preferred embodiment, a hydroxymethylated polyamide ligand may be both polymerized and crosslinked using only a single polymerization/crosslinking agent. As such, one skilled in the art may utilize these known polymerization agents and crosslinking agents in any functional combination and not depart from the scope of the present invention.

Representative examples of polyamide ligands (L) that may be hydroxymethylated and then polymerized to form polyamide ligand-containing polymeric resins that have at least three amide groups and two or more amine nitrogens separated by at least two carbons include: ethylenebis(oxyethylenenitrilo) tetraacetic acid (EGTAM), diaza-18-crown-6-tetraamide, ethylenediaminetetraacetamide-N-methylenepropanetetraamine (EDTAAMT), tris(2-aminoethyl)amine pentaamide (TRENPA), and diethylenetriaminepentaacetamide (DTPA). This list is intended only to be representative of the possible ligands that may be used, the limiting factor being

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the presence of at least three amide groups, preferably from three to eight amide groups, and at least two amine nitrogens separated by two or more carbons.

Further variations of these ligands may also be used. For example, tris(2-aminoethyl)amine pentaamide (TRENPAM) may be alkyl or aryl substituted.

5 Once polymerized, the polyamide-ligand units of the present invention form beads and/or granules which may be used for ion removal, separation, and/or concentration.

As summarized above, the present invention is drawn to a novel composition of matter comprising polyamide-containing ligand molecules 10 covalently bound to solid support materials to form the compounds of Formula 9. The present invention is also drawn to novel compositions of matter comprising polyamide ligand-containing polymeric resins as described in Formula 14. However, by utilizing these compositions, the present invention is also drawn to 15 methods for the preferential removal, separation, and/or concentration of certain desired metal ions, such as certain transition, post-transition, and alkaline earth metal ions from solution. The solution from which the desired ions may be removed may contain other metal ions or hydrogen ions present at greater concentrations than the desired ions. For example,  $Cd^{2+}$ ,  $Pb^{2+}$ , and  $Ag^+$  may be removed from acidic and or highly chelative matrices and  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Fe^{3+}$ ,  $Cu^{2+}$ , 20  $Sr^{2+}$ , and  $Ca^{2+}$  may be removed from slightly acidic to neutral pH matrices and from chelating matrices. Moreover, the above described polyamide-containing ligand molecules covalently bound to solid supports and polyamide ligand-containing polymeric resins provide means for separating ppb to ppm levels of  $Cd^{2+}$  and  $Pb^{2+}$  from concentrated acid solution by using separation techniques and 25 equipment generally known in the art. Moreover the above described structures such as those described in Formula 9 and Formula 14 provide a means for separating ppb to ppm levels of  $Cd^{2+}$  and  $Pb^{2+}$  from concentrated acid solution by using the separation techniques and equipment generally known in the art.

The method for separating and recovering desired ions is accomplished by 30 forming a complex of the desired ions with a polyamide-containing ligand which is bonded to a solid support or which is in the form of a polymeric resin.

Specifically, this is accomplished by flowing a source solution containing the desired ion(s) through a column packed with either of the polyamide-containing ligand structures in order to complex or chelate the desired metal ion(s) to the

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polyamide ligand portion of either composition, i.e., as in Formula 9 or Formula 14. Subsequently, the desired cation which is bound to the polyamide-containing ligand is released by flowing a complex-breaking receiving liquid in much smaller volume than the volume of source solution originally passed through the column. This removes and concentrates the desired ions in the receiving liquid solution by either (a) forming a stronger complex with the desired transition, post-transition or alkaline earth metal ion(s) than does the polyamide-containing ligand, or (b) temporarily forming a stronger interaction with the polyamide-containing ligand than does the desired metal ion(s), and thus, the desired metal ion(s) are quantitatively stripped from the polyamide-containing ligand structure in concentrated form in the receiving solution. The recovery of a desired metal ion(s) from the receiving liquid is accomplished by evaporation, electrowinning, precipitation, or by other known methods.

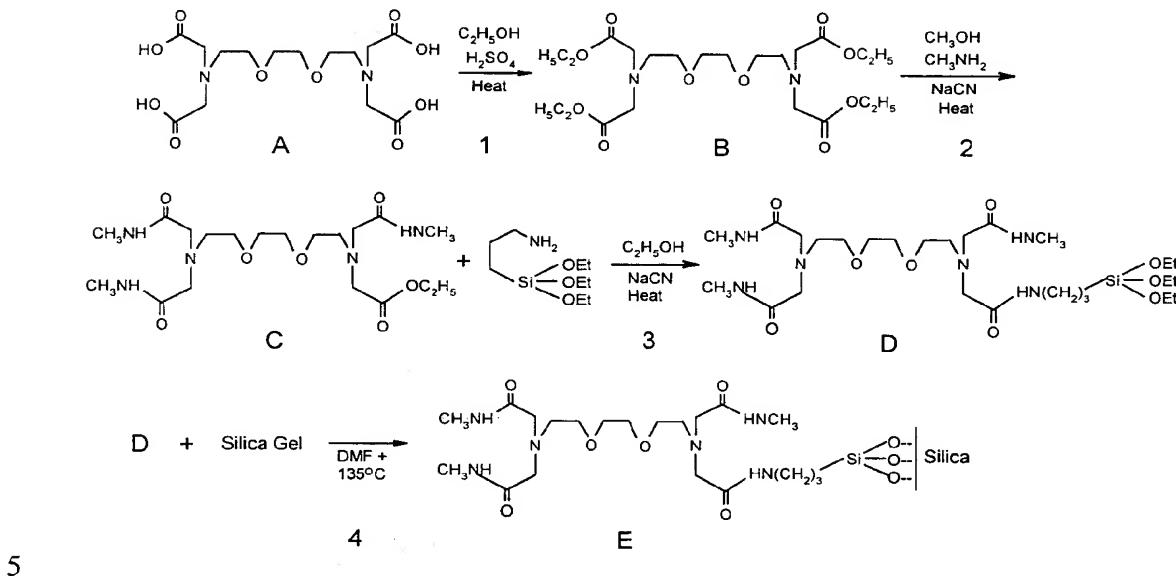
15 The following examples should not be considered as limitations of the present invention, but are merely intended to teach how to make the best known polyamide-containing solid supports based upon current experimental data.

#### EXAMPLES

##### 20 EXAMPLES 1 – 4d: SYNTHESIS OF POLYAMIDE-CONTAINING LIGATING AGENTS BONDED TO SOLID SUPPORTS

25 Examples 1 – 4D demonstrate representative structures of solid supports bonded to polyamide-containing ligands. All of these examples have several characteristics in common including: 1) each have 3 or more amide groups capable of complexing or chelating desired ions; 2) each have 2 or more amine nitrogens separated by at least 2 carbons; and 3) each has at least one solid support linkage.

**14**  
**Example 1 -** *Synthesis of dioxatetraamide [ethylene bis(oxyethylenenitrilo)tetraacetic acid (EGTAM)] attached to a silica support*



**Step 1 –** About 39.2 g of ethylene glycol-bis(β-aminoethyl ether)-

N,N,N',N'-tetraacetic acid (A) (0.1 mole), 1.5L of ethanol, and 15 mL of sulfuric acid were added to a 2 L three-neck round bottom flask. The flask was equipped with a Soxhlet extraction apparatus containing 1:1 magnesium sulfate and sodium sulfate as a drying reagent. The mixture was refluxed and the drying reagent replaced every 12 hours. After refluxing 1-2 days, the system became homogeneous. It was then refluxed for another 8 hours. Next, the system was cooled to room temperature and the ethanol was removed by evaporation. About 10% sodium carbonate aqueous solution was added to adjust the pH of the system to about 8. The resulting solution was extracted 3 times with chloroform. The organic layer was separated and dried by adding magnesium sulfate. The chloroform was then removed under reduced pressure to concentrate the product. The residue was purified by chromatography (silica gel, ethyl acetate) to afford 34.8 g (68.5%) of ethylene glycol-bis(β-aminoethyl ether)-N,N,N',N'-tetraacetic acid ethyl ester (B) as a colorless liquid. Characterization was done by NMR under the following conditions:  $^1\text{H}$  NMR (300 MHz, deuteriochloroform)  $\delta$  4.2 (q, 8 H), 3.6 (t, 12 H), 3.5 (s, 4 H), 1.2 (t, 12 H); FABMS 493 ( $\text{M}^+$ ).

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Step 2 – About 69.6 g of the tetraester (B) above, (0.14 mole), 212 mL of 2.0 M methylamine solution in methanol, and 2.08 g of sodium cyanide as a catalyst were added to a 250 mL sealed glass reactor. The mixture was refluxed for 2 days. Methanol was removed by evaporation. The residue was dissolved in 1 L of chloroform, and washed with 200 mL of water to remove the water soluble tetraacetate. The chloroform layer was separated and dried by adding magnesium sulfate. About 27.0 g of the triacetamide (C) was obtained. Characterization was done by NMR under the following conditions:  $^1\text{H}$  NMR (300 MHz, deuteriochloroform)  $\delta$  7.4 (d, 3 H), 3.5-3.2 (m, 14 H), 3.0 (s 3 H), 2.6-2.4 (m, 11 H); IR 1725  $\text{cm}^{-1}$  (carbonyl group of ester), 1660  $\text{cm}^{-1}$  (carbonyl group of amide); FABMAS 457( $\text{M}^+\text{Na}^+$ ).

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Step 3 – About 27.0 g (0.06 mole) of the triacetamide (C), 66.0 g (0.3 mole) of triethoxysilyl propyl amine, 20 mL of ethanol and a catalytic amount of sodium cyanide were added to a 250 mL sealed glass reactor. The mixture was refluxed for 2 days. The IR spectra of the reaction mixture showed that the signal (1773  $\text{cm}^{-1}$ ) from the carbonyl group of the ester disappeared and only the signal (1660  $\text{cm}^{-1}$ ) from the carbonyl group of the amide remained. The solvent was removed by a rotary evaporator. The excess triethoxysilyl propyl amine was then removed by evaporation in a vacuum chamber, 70°C/1 mm Hg. About 54.0 g of ethylene glycol-bis( $\beta$ -aminoethyl ether)-N,N,N’-[tris(N-methylacetamide)],N’-triethoxysilanepropylaminocarbonylmethylene (D) was obtained.

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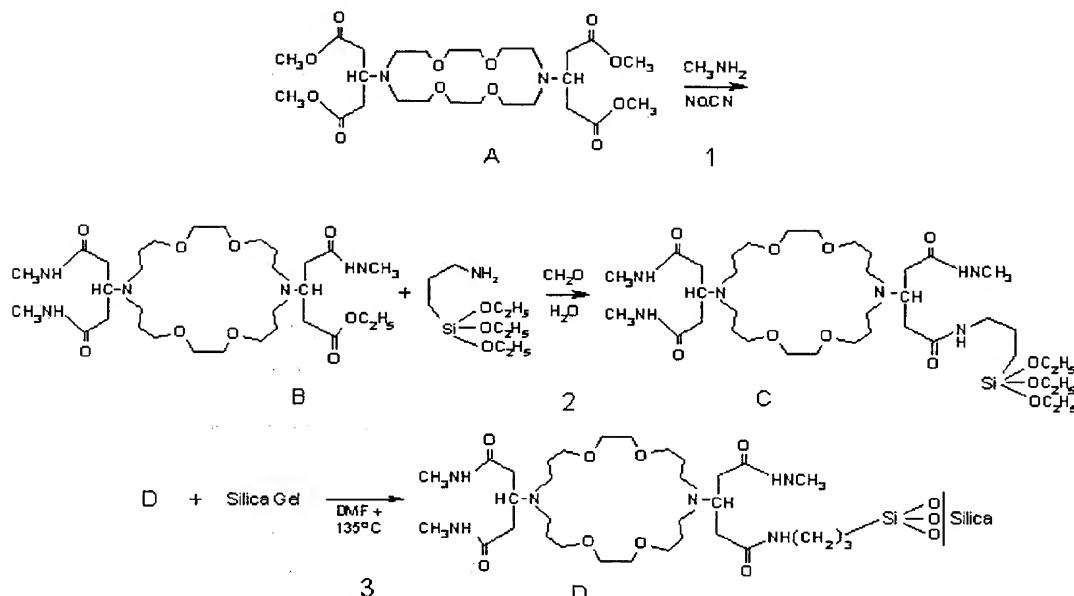
Step 4 – About 54.0 g of ethylene glycol-bis( $\beta$ -aminoethyl ether)-N,N,N’-[tris(N-methylacetamide)],N’-triethoxysilanepropylaminocarbonylmethylene (D), 54.0 g of silica gel, and 500 mL of N,N-dimethyl formamide were added to a 1L-three neck round bottom flask. The flask was equipped with a mechanical stirrer, a condenser and a thermometer. The temperature of the mixture was maintained at 135°C. After stirring for 2 days, the reaction mixture was filtered. The resulting tetraamide ligand functionalized silica gel (E) was washed with methanol several times then dried in a vacuum oven at 50-60°C for 6 hours.

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About 71.0 g of product E was obtained.

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Example 2 - <sup>16</sup> *Synthesis of diaza-18-crown-6-tetraamide attached to a silica solid support*



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Tetraester of diaza-18-crown-6 prepared as published: de Jong et. al., J. Chem. Soc., 102 (1983), pg. 164.

Step 1 – About 2.61 g of the 7,16-bis(dicarboxymethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane tetramethyl ester (A), 18 ml of 1.0 M methylamine solution in methanol and 0.1g of sodium cyanide as a catalyst was added to a 25 ml sealed glass reactor. The mixture was refluxed for 2 days. Methanol was removed by evaporation. The residue was dissolved in 0.1 L of chloroform and washed with 20 mL of water. The chloroform layer was separated and dried by adding magnesium sulfate. About 2.2 g of product B was obtained.

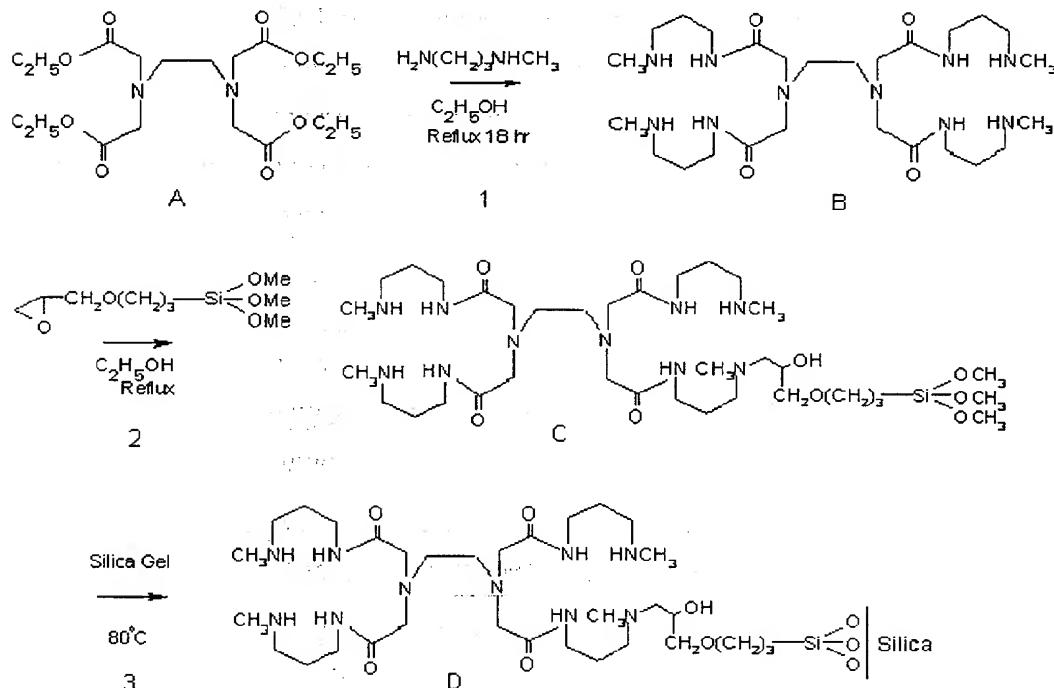
Step 2 – About 2 g of the triacetamide (B) from Step 1, 2.7 g (0.015 mole) of triethoxysilyl propyl amine, 20 mL of ethanol, and a catalytic amount of sodium cyanide were added to a 25 mL sealed glass reactor. The mixture was refluxed for 2 days. The IR spectra of the reaction mixture showed that the signal (1773 cm<sup>-1</sup>) from carbonyl group of ester disappeared and only the signal (1660 cm<sup>-1</sup>) from the carbonyl group of amide remained. The solvent was then

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removed by a rotary evaporator and the excess triethoxysilyl propyl amine was then removed by evaporation in a vacuum chamber (70°C/1 mm Hg). About 2.1 g of C was obtained.

Step 3 – About 2.2 g of the product (C) from Step 2, 5.0 g of silica gel, and 50 mL of N,N-dimethyl formamide were added to a 1 L-three neck round bottom flask. The flask was equipped with a mechanical stirrer, a condenser and a thermometer. The temperature of the mixture was maintained at 135°C. After stirring for 2 days, the reaction mixture was filtered. The resulting tetraamide ligand functionalized silica gel was washed with methanol several times then dried in a vacuum oven at 50-60°C for 6 hours. About 5.2 g of the product was obtained (D).

Example 3 – *Synthesis of ethylenediaminetetraacetamide-n-methylenepropanetetraamine (EDTAAMT) attached to a silica support*



Step 1 – About 10 g (75 mMole) of the tetraethyl acetate of ethylenediaminetetraacetic acid (ethyl-EDTA) (A) was dissolved in 200 mL of

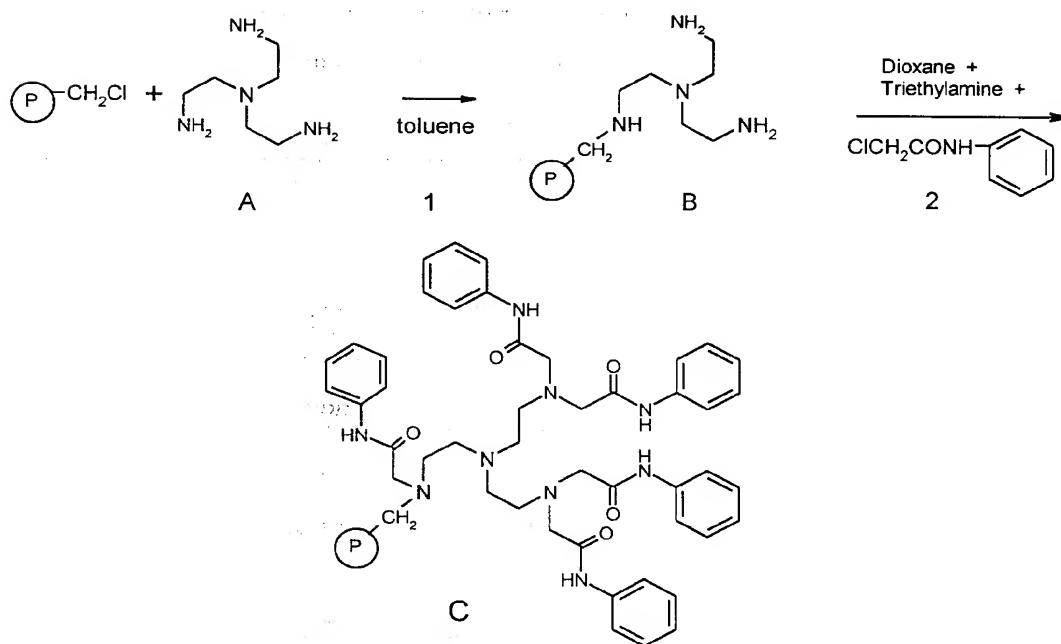
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ethyl alcohol with 88g (1 mole) of N-methyl-1,3-propanediamine and refluxed for 18 hours forming compound B above. The ethyl alcohol and excess diamine was evaporated under vacuum. Additional trace of diamine was evaporated under high vacuum.

5        Step 2 – To the above compound (B) 5.9 g (25mmole) of 3-glycidoxypyropyltrimethoxysilane and 100mL of ethyl alcohol were added. The mixture was refluxed for 3 hours forming compound C above.

10      Step 3 – About 48 g of silica gel was added and the mixture (C) and was stirred at 78°C overnight. The product was filtered, washed with ethyl alcohol and dried in a vacuum oven forming a tetraamide ligand functionalized silica gel (D).

15      Example 4A – *Synthesis of phenyl substituted tris(2-aminoethyl)amine pentaamide (TRENPAM) attached to a polystyrene solid support*



20      Step 1 – About 2 g of chloromethyl polystyrene, 2% DVB (Merrifield resin) was mixed with 10 g of tris(2-aminoethyl)amine (TREN), and 15 mL of toluene. The reaction mixture was kept at 80°C overnight. The resulting

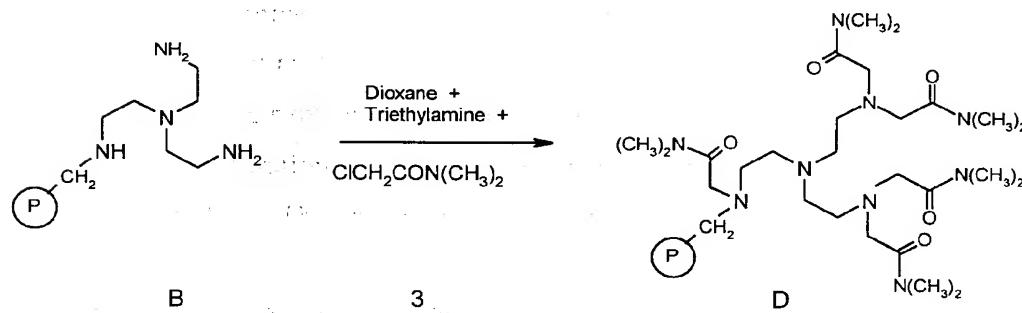
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functionalized polystyrene solid support (B) was filtered and washed in order with methanol, water, methanol, and then dried under vacuum at 50°C.

Step 2 – About 2 g of the derivative of polystyrene functionalized with trisamine (B), was mixed with 3 g of N-phenylchloroacetamide in 25 mL of dioxane and 3 mL of triethylamine. The reaction mixture was mixed overnight at 80°C. The resulting pentaamide ligand functionalized polystyrene support (C) was removed by filtration, washed with dioxane and methanol and dried under the vacuum at 50°C. The product yield was about 2 g.

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Example 4B – Synthesis of dimethyl substituted tris(2-aminoethyl)amine pentaamide (TRENPAM) attached to a polystyrene solid support

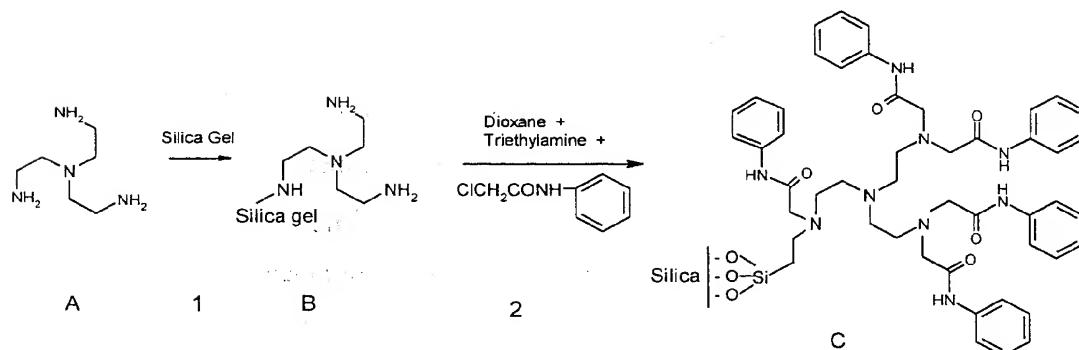


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Step 3 – The dimethyl analog of C above (D) was prepared using the same procedures as above with the substitution of 3 g of N,N-dimethylchloroacetamide in place of N-phenylchloroacetamide in Example 5a, Step 2.

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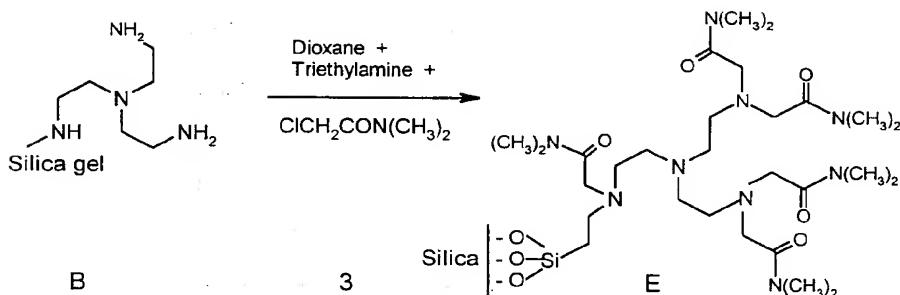
Example 4C – Synthesis of phenyl substituted tris(2-aminoethyl)amine pentaamide (TRENPAM) attached to a silica support



Step 1 – Tris(2-aminoethyl)amine was attached to silica gel using techniques described in U.S. Patent 4,952,321.

5           Step 2 – About 2 g of the tris(2-aminoethyl)amine functionalized silica gel (B) was added to 25 mL of 1,4-dioxane solution containing 3 g of N-phenylchloroacetamide and 1.8 g of triethylamine. The reaction mixture was mixed overnight at 80°C. The resulting pentaamide ligand functionalized silica gel (C) was filtered and washed with 1,4-dioxane and methanol and dried under 10 vacuum at 50°C. The product yield was about 2.3 g.

Example 4D – *Synthesis of dimethyl substituted tris(1-aminoethyl)amine pentaamide (TRENPAM) attached to a silica support*



15           Step 3 – Functionalized silica gel (E) was prepared using the same procedure as Example 5C, Step 2, above with the substitution of 3 g of N,N-dimethylchloroacetamide for N-phenylchloroacetamide.

20           **EXAMPLES 5 – 8: CONCENTRATION OF DESIRED IONS WITH POLYAMIDE-CONTAINING LIGATING AGENTS BONDED TO SOLID SUPPORTS**

The following examples demonstrate how the polyamide-containing ligating agents of Formula 9 may be used to remove and concentrate desired ions.

25           Example 5 – *Separation using EGTAM attached to silica support*

About 0.05 g of the EGTAM attached to silica as shown in Example 1

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was placed in a column. A 25°C, 10mL source solution consisting of 1M KCl, 20 ppm Cu(II), 20 ppm Pb(II) and 0.05 ppm Cd(II) in H<sub>2</sub>O was drawn through the column. A 5mL aqueous solution of 0.2 M glycine and 0.4 M potassium citrate at 25°C was then passed through the column to wash out the loading solution remaining in the column. The Cd(II) was then eluted with 5 mL of 25°C, 0.7 M glycine. Analysis of the above solutions by Atomic Absorption Spectroscopy (AA) showed that greater than 98% of the Cd(II) originally in the source solution described above was in the receiving solution. Furthermore, the Cu, Fe, and Pb levels in the receiving liquid were less than 1 ppm.

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Example 6 - Separations using EGTAM attached to solid support

About 1.0 g. of the EGTAM attached to silica as shown in Example 1 was placed in a column. At 25°C, a 3 mL source solution of 3204 ppm Cd(II) and 65 g/L Zn in pH 2 water plus H<sub>2</sub>SO<sub>4</sub> was drawn through the column. A 4 mL aqueous solution of 0.01 M H<sub>2</sub>SO<sub>4</sub> at 25°C was then passed through the column to wash out the loading solution remaining in the column. The Cd(II) was then eluted with 1 mL of 25°C, 1 M H<sub>2</sub>SO<sub>4</sub>. Analysis of the above solutions by Inductively Coupled Plasma Spectroscopy (ICP) showed that 25% of the Cd(II) from the feed was in the receiving solution for a cadmium level of 2400 ppm and the Zn level in the receiving solution was only 40 ppm.

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Example 7 - Separations using EDTAM attached to silica solid support

In this example 0.1 g of the EDTAM attached to silica gel as shown in Example 4B was placed in a column. A 25°C, 10 mL source solution of 65 ppm Cu in 0.01 M HCl was drawn through the column. The Cu was then eluted with 5 mL of 25°C, 1 M H<sub>2</sub>SO<sub>4</sub>. Analysis of the above solutions by Inductively Coupled Plasma Spectroscopy (ICP) showed that greater than 95% of the Cu originally in the 10 mL solution described above was in the 5 mL receiving solution. Furthermore, a full loading curve experiment with 100 mL of the same source solution resulted in a subsequent removal of 0.02 mMole Cu<sup>2+</sup> from the receiving solution.

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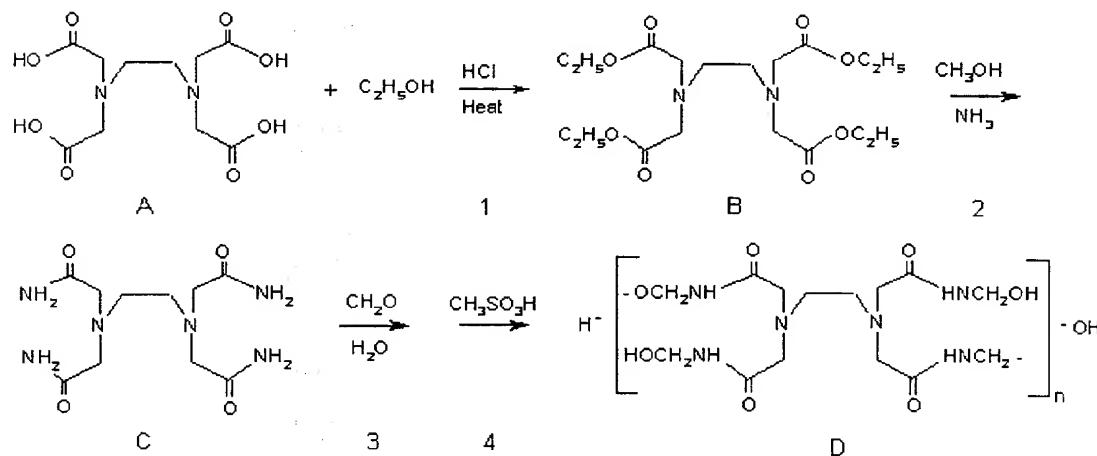
Example 8 - *Separations using tris amine amide attached to polystyrene solid support*

About 0.1 g of the tris amine amide as shown in Example 4B was placed in a column. A 25°C, 1 mL source solution of 290 ppm Pb(II) and 100 g/L Ag(I) in 0.1 M HNO<sub>3</sub> was drawn through the column. A 2 mL aqueous solution at 25°C was then passed through the column to wash out the loading solution remaining in the column. The Pb(II) was then eluted with 2 mL of 25°C, 5 M HNO<sub>3</sub>. Analysis of the above solutions by Atomic Adsorption Spectroscopy (AA) showed that greater than 98% of the Pb(II) originally in the 1 mL solution described above was in the 2 mL receiving solution. Furthermore, the Ag(I) level in the receiving liquid was less than 1 ppm.

## EXAMPLES 9 AND 10: SYNTHESIS OF POLYAMIDE-CONTAINING POLYMERIC RESINS

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Example 9 – Synthesis of ethylenediaminetetraacetamide (EDTAM) and polymerization forming a polymeric resin



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Step 1 – About 140 g (0.48 mole) of ethylenediaminetetraacetic acid (EDTA) (A) and 600 mL of ethyl alcohol were placed in a flask equipped with a Soxhlet extraction apparatus and refluxed while HCl gas was continuously bubbled through the system. After the mixture became homogeneous, it was

refluxed for another 5 hours. The ethanol was then removed by evaporation. A 10% sodium carbonate aqueous solution was added to adjust the pH of the solution to about 8. The solution was then extracted with diethyl ether. The diethyl ether organic layer was separated, dried by adding sodium sulfate and concentrated under reduced pressure. About 153g (79% of theoretical) of the tetraester (B) was obtained after purification by column chromatography (silica, ethyl acetate). Purity was determined by NMR giving the following values: <sup>1</sup>H NMR (300 MHz, DCCl<sub>3</sub>, [deuteriochloroform]) δ 4.2 (q,8H), 3.6 (s,8H), 2.9 (s4H), 1.3 (t,12H); FABMS 404(M<sup>+</sup>).

10        Step 2 – About 10 g (25mmole) of tetraester (B) was dissolved in 30 mL of methyl alcohol and combined with 200 mL of 7N ammonia solution in methyl alcohol. The mixture was stirred for 5 days at room temperature. A white precipitate formed that was filtered and washed with methyl alcohol. The precipitate was then dried in a vacuum oven. About 5 g of EDTAA (C) was  
15        formed.

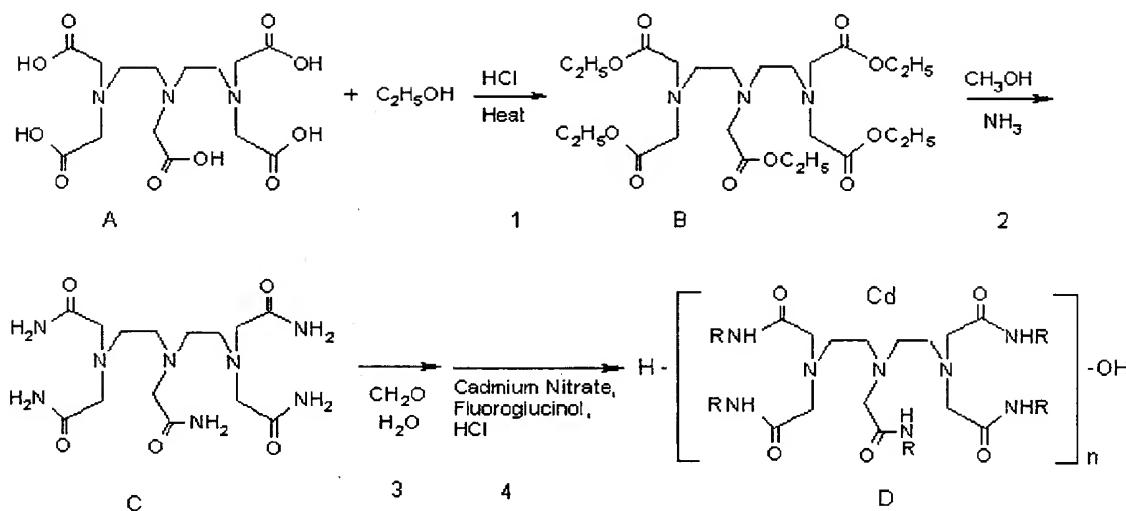
20        Step 3 – About 5 g of EDTAA (C), was dissolved in 100 mL of water and combined with a solution containing 2 g of *para*formaldehyde in 8mL of water. The system was stirred at room temperature for 3 hours. The water was then evaporated and the hydroxymethylated tetraacetamide residue was dried under a vacuum using phosphorous pentaoxide.

25        Step 4 – About 2 g of the hydroxymethylated tetraacetamide obtained in Step 3 was treated with 10 mL of methanesulfonic acid at room temperature for 2 hours. A polymeric mass (D) was formed which was filtered, washed with water and dried under a vacuum at 50°C using phosphorous pentaoxide. About 2 g of the EDTAM polymeric resin (D) was obtained.

30        The EDTAM polymeric resin structure (D) illustrates an essentially linear polymeric resin. However, this structure may be further polymerized or crosslinked using additional amounts of the polymerization agent, an additional polymerization agent, or a crosslinking agent. The structure of such a crosslinked resin structure would be difficult to ascertain as it would depend on the crosslinking agent, the number of amide groups entering into the crosslinking reaction, the degree of polymerization, and other variables known by those skilled in the art.

Example 10 – *Synthesis of diethylenetriaminepentaacamide (DTPAM) and polymerization forming a crosslinked polymeric resin*

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Step 1 - About 189 g (0.48 moles) of tris(2-aminoethyl)pentaacetic acid (A) and 1000 mL of ethyl alcohol were placed in a flask equipped with a Soxhlet extraction apparatus and refluxed while HCl gas was continuously bubbled through the system. After the mixture became homogeneous, it was refluxed for another 7 hours. The ethanol was then removed by evaporation. A 10% sodium carbonate aqueous solution was added to adjust the pH of the solution to about 8. The solution was then extracted with diethyl ether. The diethyl ether organic layer was separated, dried by adding sodium sulfate and concentrated under reduced pressure. About 192 g (75% of theoretical) of the pentaester (B), was obtained after purification by column chromatography (silica, ethyl acetate). Purity was determined by NMR giving the following values:  $^1\text{H}$  NMR (300 MHz,  $\text{DCCl}_3$ , [deuteriochloroform])  $\delta$  4.2 (q, 10H), 3.6 (mm, 10H), 3.2 (m, 4H), 3.0 (m, 4H), 1.3 (t, 15H), FABMS  $537(\text{M}^+)$ .

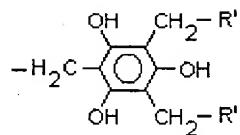
Step 2 – About 13 g (25mmole) of the pentaester (B) was dissolved in 40 mL of methyl alcohol and combined with 200 mL of 7 N ammonia solution in methyl alcohol. The mixture was stirred for 6 days at room temperature. A white

precipitate formed that was filtered and washed with methyl alcohol. The precipitate was then dried in a vacuum oven. About 6 g of DTPAA (C) was formed.

5           Step 3 – The hydroxymethylated pentaacetamide derivative of DTPAA was prepared by dissolving DTPAA (C) in water and combining with an aqueous solution of paraformaldehyde. The system was stirred for 3 hours at room temperature.

10           Step 4 – About 3 g (5.7mmole) of cadmium nitrate tetrahydrate was dissolved in 50 mL of water and added to the hydroxymethylated compound solution of Step 3. A cadmium complex was allowed to form by stirring the complex for 20 minutes at room temperature. The complex was used as a template for polymerization. About 1.5 g of fluoroglucinol in 20 mL of ethyl alcohol and 2 mL of concentrated hydrochloric acid were added to the solution. The solution was kept at a temperature of 60°C for 3 hours then stirred at room 15 temperature overnight. A polymeric resin (D) formed which was filtered, washed with water then methanol and dried under a vacuum at 50°C using phosphorous pentaoxide. About 4.1 g of the DTPAM polymeric resin (D) was obtained.

20           In the present example, paraformaldehyde is used to prepare the hydroxymethylated pentaacetamide derivative of DTPAA. If used in excess, the paraformaldehyde may initiate some polymerization. However, in the present example, the bulk of the polymerization and/or crosslinking is a result of the addition of the fluoroglucinol. Therefore, in Formula D of this example, R may represents either a hydroxymethyl group, i.e., CH<sub>2</sub>OH, a resulting group from any polymerization that occurs, or the following crosslinking agent which is a derived 25 from fluoroglucinol:



where R' is either an –OH group or another polyamide ligand unit on the polymer itself, i.e., crosslinking. If both of the R' variables are –OH, then there is no crosslinking. Therefore, it is preferably that at least one R' group is involved in

crosslinking, i.e., not an -OH group. Further, at least one of the R groups of Formula D must be involved in the polymerization or crosslinking, preferably from two to five.

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#### EXAMPLE 11: CONCENTRATION OF DESIRED IONS WITH POLYAMIDE-CONTAINING POLYMERIC RESINS

The following example demonstrates how the polyamide-containing polymeric resins of Formula 14 may be used to remove and concentrate desired ions

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##### Example 11 – Separations using DTPAM polymeric resins

In this example, 0.1 g of the DTPAM polymer of Example 10 was placed in a packed column. A 75 mL source solution containing 2 ppm (parts per million) of Sr<sup>2+</sup> in 0.05 M KCl, 0.1 M sodium acetate, and 0.01 M acetic acid was 15 passed through the column. About 2 mL of water was then passed through the column to wash out the remaining loading solution. Next, the Sr<sup>2+</sup> was eluted with 1 mL of 0.5 M H<sub>2</sub>SO<sub>4</sub>. Analysis of the above solutions by Atomic Adsorption Spectroscopy (AA) showed that greater than 99% of the Sr<sup>2+</sup> originally present in the source solution described above was separated into the 1 20 mL receiving solution. Furthermore, the K<sup>+</sup> and Na<sup>+</sup> levels in the receiving liquid were less than 1 ppm.

Although the invention has been described and illustrated with reference to certain specific embodiments falling within the scope of Formula 14, other embodiments may be practiced. For example, other analogs of these polyamide-containing ligating compounds and methods of using the same are also within the 25 scope of the invention. The invention is therefore limited only in scope by the following claims and functional equivalents thereof.

30

CLAIMS

We claim:

1. A composition for selectively binding metal ions comprising a polyamide-containing ligand covalently bonded to a particulate solid support through a hydrophilic spacer having the formula:

SS-A-X-L

wherein SS is a particulate solid support, A is a covalent linkage mechanism, X is a hydrophilic spacer grouping, and L is polyamide-containing ligand with the proviso that when SS is a particulate organic polymer, A-X may be combined as a single covalent linkage.

2. A composition according to claim 1 wherein said polyamide-containing ligand has three or more amide groups and two or more amine nitrogens separated by at least two carbons.

3. A composition according to claims 2 wherein said polyamide-containing ligand is selected from the group consisting of ethylene bis(oxyethylenenitrilo)tetraacetic acid (EGTAM), diaza-18-crown-6-tetraamide, ethylenediaminetetraacetamide-N-methylenepropanetetraamine (EDTAAMT), tris(2-aminoethyl)amine pentaamide (TRENPA), and diethylenetriaminepentaacetamide (DTPA).

4. A composition according to Claims 1 to 3 wherein SS is a inorganic solid support selected from the group consisting of sand, silica gel, glass, glass fibers, alumina, zirconia, titania, and nickel oxide and combinations thereof.

5. A composition according to Claims 1 to 3 wherein A is a member selected from the group consisting of  $Si(Z,Z)-O$ , wherein Z can independently represent members selected from the group consisting of Cl, Br, I, lower alkyl, lower alkoxy, substituted lower alkyl or substituted lower alkoxy and O-SS.

6. A composition according to Claims 1 to 3 wherein X is a member represented by the formula:



wherein  $\text{R}^1$  is a member selected from the group consisting of H, SH, OH, lower alkyl, and aryl; a is an integer from 2 to about 10; and b is 0 or 1.

5        7. A composition according to Claim 6 wherein the - $\text{CH}_2$ - group of said spacer (X) which is most distal to said solid support (SS) is covalently bonded to an amide group of said ligand (L) wherein said amide group is represented by the formula:



10      where m is 0 or 1; and n is 0 or 1 with the proviso that when m is 1, n is 0 and when m is 0, n is 1.

15      8. A composition according to Claim 6 wherein the - $\text{CH}_2$ - group of said spacer (X) which is most distal to said solid support (SS) is covalently bonded to an amine nitrogen.

20      9.      A composition according to Claims 1 to 3 wherein SS is a particulate polymeric organic solid support matrix selected from the group consisting of polyacrylate, polystyrene, and polyphenol and combinations thereof.

10.      A composition according to Claim 9 wherein A and X combined are represented by the formula:



25      where y is an integer of 0 or 1; x and z are independently integers between 0 and 10; and Y is member selected from the group consisting of O, S, C=N, CO, CONH, CSNH, COO, CSO, NH, NR, SO, SO<sub>2</sub>, SO<sub>2</sub>NH, C<sub>6</sub>H<sub>4</sub> and CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> where R is lower alkyl with the proviso that at least one of x, y and z must be at least 1.

30      11. A polyamide ligand-containing polymeric resin which is a reaction product of a hydroxymethylated polyamide ligand and one or more agents selected from the group consisting of polymerization agents, crosslinking agents,

and combinations thereof, said polymeric resin being comprised of from 10 to 50,000 polyamide ligand units.

12. A polyamide ligand-containing polymeric resin according to Claim 5 11 wherein each of said polyamide ligand units has three or more amide groups and two or more amine nitrogens separated by at least two carbons.

13. A polyamide ligand-containing polymeric resin according to Claim 10 12 wherein each of said polyamide ligand units has from three to eight amide groups.

14. A polyamide ligand-containing polymeric resin according to Claims 15 11 to 13 wherein at least one amide group of each of said polyamide ligand units is polymerized or crosslinked to another polyamide ligand unit by a polymerization agent or a crosslinking agent.

15. A polyamide ligand-containing polymeric resin according to Claim 20 14 wherein from two to eight amide groups of said polyamide ligand unit are polymerized or crosslinked to one or more polyamide ligand units by a polymerization agent or a crosslinking agent.

16. A polyamide ligand-containing polymeric resin according to Claim 14 25 wherein said polymerization agent is selected from the group consisting of bisaldehydes, polyaldehydes, dihalogens, polyhalogens, dihalogens of diacids, polyhalogens of polyacids, diesters, polyesters, anhydrides of acids, diepoxides, polyepoxides, and combinations thereof.

17. A polyamide ligand-containing polymeric resin according to Claim 14 30 wherein said crosslinking agent is selected from the group consisting of phenols, resorcinols, fluoroglucinols, aromatic amines, aliphatic amines, pyrroles, indoles, nitrates, esters, ketones, nitriles, and combinations thereof.

18. A polyamide ligand-containing polymeric resin according to Claim 14 wherein said hydroxymethylated polyamide ligand is derived from a member

selected from the group consisting of ethylene bis(oxyethylenenitrilo)tetraacetic acid (EGTAM), diaza-18-crown-6-tetraamide, ethylenediaminetetraacetamide-N-methylenepropanetetraamine (EDTAAMT), tris(2-aminoethyl)amine pentaamide (TRENPAM), diethylenetriaminepentaacetamide (DTPAM), and combinations thereof.

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19. A polyamide ligand-containing polymeric resin according to Claim 18 wherein said hydroxymethylated polyamide ligand is derived from ethylene bis(oxyethylenenitrilo)tetraacetic acid (EGTAM).

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20. A polyamide ligand-containing polymeric resin according to Claim 18 wherein said hydroxymethylated polyamide ligand is derived from diaza-18-crown-6-tetraamide.

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21. A polyamide ligand-containing polymeric resin according to Claim 18 wherein said hydroxymethylated polyamide ligand is derived from ethylenediaminetetraacetamide-N-methylenepropanetetraamine (EDTAAMT).

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22. A polyamide ligand-containing polymeric resin according to Claim 18 wherein said hydroxymethylated polyamide ligand is derived from tris(2-aminoethyl)amine pentaamide (TRENPAM).

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23. A polyamide ligand-containing polymeric resin according to Claim 18 wherein said hydroxymethylated polyamide ligand is derived from diethylenetriaminepentaacetamide (DTPAM).

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24. A method for concentrating, removing, or separating selected ions from a source solution comprising the steps of:

(a) contacting said source solution having a first volume with a

composition comprising a polyamide-containing ligand covalently bonded to a particulate solid support through a hydrophilic spacer having the formula:

SS-A-X-L

where SS is a particulate solid support, A is a covalent linkage mechanism, X is a hydrophilic spacer grouping, L is a polyamide-containing ligand with the proviso

that when SS is a particulate organic polymer, A-X may be combined as a single covalent linkage, and wherein said L portion of the composition has an affinity for said selected ions such as to form a complex between said selected ions and said L portion of said composition;

5 (b) removing the source solution from contact with said composition to which said selected ions have been complexed; and

10 (c) contacting said composition having said selected ions complexed thereto with a smaller volume of an aqueous receiving solution in which said selected ions are either soluble or which has greater affinity for such selected ions than does the ligand portion of the composition thereby quantitatively stripping such selected ions from the ligand and recovering said selected ions in concentrated form in said receiving solution.

15 25. A method for removing, separating, or concentrating selected ions from a source solution comprising the steps of:

20 (a) contacting said source solution having a first volume with a polyamide ligand-containing polymeric resin which is a reaction product of a hydroxymethylated polyamide ligand and one or more agents selected from the group consisting of polymerization agents, crosslinking agents, and combinations thereof, said polymeric resin being comprised of from 10 to 50,000 polyamide ligand units, and wherein said polymeric resin has an affinity for said selected ions such as to form a complex between said selected ions and said polymeric resin;

25 (b) removing the source solution from contact with said polymeric resin to which said selected ions have been complexed; and

30 (c) contacting said polymeric resin having said selected ions complexed thereto with a smaller volume of an aqueous receiving solution in which said selected ions are either soluble, or which has greater affinity for such selected ions than does the polymeric resin, thereby quantitatively stripping such selected ions from the ligand and recovering said selected ions in concentrated form in said receiving solution.

26. A method according to Claims 24 or 25 wherein said selected ion is a member selected from the group consisting of transition, post-transition, and

alkaline earth metal ions.

27. A method according to Claims 26 wherein said selected ions are transition metal ions selected from the group consisting of  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , 5  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ , and combinations thereof.

28. A method according to Claim 26 wherein said post-transition metal ion is  $\text{Pb}^{2+}$ .

10 29. A method according to Claim 26 wherein said selected ions are alkaline earth metal ions selected from the group consisting of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and combinations thereof.

15 30. A method according to claim 24 wherein said polyamide-containing ligand has three or more amide groups and two or more amine nitrogens separated by at least two carbons.

20 31. A method according to Claim 25 wherein each of said polyamide ligand units has three or more amide groups and two or more amine nitrogens separated by at least two carbons.

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**AMENDED CLAIMS**

[received by the International Bureau on 16 February 2001 (16.02.01);  
original claims 1-31 replaced by new claims 1-31 (6pages)]

**CLAIMS**

We claim:

1. A composition for selectively binding metal ions comprising a polyamide-containing ligand covalently bonded to a particulate solid support through a hydrophilic spacer having the formula:



wherein SS is a particulate solid support, A is a covalent linkage mechanism, X is a hydrophilic spacer grouping, and L is polyamide-containing ligand with the proviso that when SS is a particulate organic polymer, A-X may be combined as a single covalent linkage.

2. A composition according to claim 1 wherein said polyamide-containing ligand has three or more amide groups and two or more amine nitrogens separated by at least two carbons.

3. A composition according to claims 2 wherein said polyamide-containing ligand is selected from the group consisting of ethylene bis(oxyethylenenitrilo)tetraacetic acid (EGTAM), diaza-18-crown-6-tetraamide, ethylenediaminetetraacetamide-N-methylenepropanetetraamine (EDTAAMT), tris(2-aminoethyl)amine pentaamide (TRENPAAM), and diethylenetriaminepentaacetamide (DTPAM).

4. A composition according to Claims 1, 2, or 3 wherein SS is a inorganic solid support selected from the group consisting of sand, silica gel, glass, glass fibers, alumina, zirconia, titania, and nickel oxide and combinations thereof.

5. A composition according to Claims 1, 2, or 3 wherein A is a member selected from the group consisting of  $\text{Si}(Z,Z)\text{-O}$ , wherein Z can independently represent members selected from the group consisting of Cl, Br, I, lower alkyl, lower alkoxy, substituted lower alkyl or substituted lower alkoxy and  $\text{O-SS}$ .

6. A composition according to Claims 1, 2, or 3 wherein X is a

member represented by the formula:



wherein  $R^1$  is a member selected from the group consisting of H, SH, OH, lower alkyl, and aryl; a is an integer from 2 to about 10; and b is 0 or 1.

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7. A composition according to Claim 6 wherein the  $-\text{CH}_2-$  group of said spacer (X) which is most distal to said solid support (SS) is covalently bonded to an amide group of said ligand (L) wherein said amide group is represented by the formula:

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where m is 0 or 1; and n is 0 or 1 with the proviso that when m is 1, n is 0 and when m is 0, n is 1.

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8. A composition according to Claim 6 wherein the  $-\text{CH}_2-$  group of said spacer (X) which is most distal to said solid support (SS) is covalently bonded to an amine nitrogen.

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9. A composition according to Claims 1, 2, or 3 wherein SS is a particulate polymeric organic solid support matrix selected from the group consisting of polyacrylate, polystyrene, and polyphenol and combinations thereof.

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10. A composition according to Claim 9 wherein A and X combined are represented by the formula:



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where y is an integer of 0 or 1; x and z are independently integers between 0 and 10; and Y is member selected from the group consisting of O, S, C=N, CO, CONH, CSNH, COO, CSO, NH, NR, SO, SO<sub>2</sub>, SO<sub>2</sub>NH, C<sub>6</sub>H<sub>4</sub> and CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> where R is lower alkyl with the proviso that at least one of x, y and z must be at least 1.

11. A polyamide ligand-containing polymeric resin which is a reaction product of a hydroxymethylated polyamide ligand and one or more agents selected from the group consisting of polymerization agents, crosslinking agents,

and combinations thereof, said polymeric resin being comprised of from 10 to 50,000 polyamide ligand units.

5 12. A polyamide ligand-containing polymeric resin according to Claim 11 wherein each of said polyamide ligand units has three or more amide groups and two or more amine nitrogens separated by at least two carbons.

10 13. A polyamide ligand-containing polymeric resin according to Claim 12 wherein each of said polyamide ligand units has from three to eight amide groups.

15 14. A polyamide ligand-containing polymeric resin according to Claims 11, 12, or 13 wherein at least one amide group of each of said polyamide ligand units is polymerized or crosslinked to another polyamide ligand unit by a polymerization agent or a crosslinking agent.

20 15. A polyamide ligand-containing polymeric resin according to Claim 14 wherein from two to eight amide groups of said polyamide ligand unit are polymerized or crosslinked to one or more polyamide ligand units by a polymerization agent or a crosslinking agent.

25 16. A polyamide ligand-containing polymeric resin according to Claim 14 wherein said polymerization agent is selected from the group consisting of bisaldehydes, polyaldehydes, dihalogens, polyhalogens, dihalogens of diacids, polyhalogens of polyacids, diesters, polyesters, anhydrides of acids, diepoxides, polyepoxides, and combinations thereof.

30 17. A polyamide ligand-containing polymeric resin according to Claim 14 wherein said crosslinking agent is selected from the group consisting of phenols, resorcinols, fluoroglucinols, aromatic amines, aliphatic amines, pyrroles, indoles, nitrates, esters, ketones, nitriles, and combinations thereof.

18. A polyamide ligand-containing polymeric resin according to Claim 14 wherein said hydroxymethylated polyamide ligand is derived from a member

selected from the group consisting of ethylene bis(oxyethylenenitrilo)tetraacetic acid (EGTAM), diaza-18-crown-6-tetraamide, ethylenediaminetetraacetamide-N-methylenepropanetetraamine (EDTAAMT), tris(2-aminoethyl)amine pentaamide (TREN PAM), diethylenetriaminepentaacetamide (DTPAM), and combinations thereof.

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19. A polyamide ligand-containing polymeric resin according to Claim 18 wherein said hydroxymethylated polyamide ligand is derived from ethylene bis(oxyethylenenitrilo)tetraacetic acid (EGTAM).

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20. A polyamide ligand-containing polymeric resin according to Claim 18 wherein said hydroxymethylated polyamide ligand is derived from diaza-18-crown-6-tetraamide.

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21. A polyamide ligand-containing polymeric resin according to Claim 18 wherein said hydroxymethylated polyamide ligand is derived from ethylenediaminetetraacetamide-N-methylenepropanetetraamine (EDTAAMT).

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22. A polyamide ligand-containing polymeric resin according to Claim 18 wherein said hydroxymethylated polyamide ligand is derived from tris(2-aminoethyl)amine pentaamide (TREN PAM).

25

23. A polyamide ligand-containing polymeric resin according to Claim 18 wherein said hydroxymethylated polyamide ligand is derived from diethylenetriaminepentaacetamide (DTPAM).

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24. A method for concentrating, removing, or separating selected ions from a source solution comprising the steps of:

(a) contacting said source solution having a first volume with a composition comprising a polyamide-containing ligand covalently bonded to a particulate solid support through a hydrophilic spacer having the formula:

SS-A-X-L

where SS is a particulate solid support, A is a covalent linkage mechanism, X is a hydrophilic spacer grouping, L is a polyamide-containing ligand with the proviso

that when SS is a particulate organic polymer, A-X may be combined as a single covalent linkage, and wherein said L portion of the composition has an affinity for said selected ions such as to form a complex between said selected ions and said L portion of said composition;

5 (b) removing the source solution from contact with said composition to which said selected ions have been complexed; and

10 (c) contacting said composition having said selected ions complexed thereto with a smaller volume of an aqueous receiving solution in which said selected ions are either soluble or which has greater affinity for such selected ions than does the ligand portion of the composition thereby quantitatively stripping such selected ions from the ligand and recovering said selected ions in concentrated form in said receiving solution.

15 25. A method for removing, separating, or concentrating selected ions from a source solution comprising the steps of:

20 (a) contacting said source solution having a first volume with a polyamide ligand-containing polymeric resin which is a reaction product of a hydroxymethylated polyamide ligand and one or more agents selected from the group consisting of polymerization agents, crosslinking agents, and combinations thereof, said polymeric resin being comprised of from 10 to 50,000 polyamide ligand units, and wherein said polymeric resin has an affinity for said selected ions such as to form a complex between said selected ions and said polymeric resin;

25 (b) removing the source solution from contact with said polymeric resin to which said selected ions have been complexed; and

30 (c) contacting said polymeric resin having said selected ions complexed thereto with a smaller volume of an aqueous receiving solution in which said selected ions are either soluble, or which has greater affinity for such selected ions than does the polymeric resin, thereby quantitatively stripping such selected ions from the ligand and recovering said selected ions in concentrated form in said receiving solution.

26. A method according to Claims 24 or 25 wherein said selected ion is a member selected from the group consisting of transition, post-transition, and

alkaline earth metal ions.

27. A method according to Claims 26 wherein said selected ions are transition metal ions selected from the group consisting of  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  
5  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ , and combinations thereof.

28. A method according to Claim 26 wherein said post-transition metal ion is  $\text{Pb}^{2+}$ .

10 29. A method according to Claim 26 wherein said selected ions are alkaline earth metal ions selected from the group consisting of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and combinations thereof.

15 30. A method according to claim 24 wherein said polyamide-containing ligand has three or more amide groups and two or more amine nitrogens separated by at least two carbons.

20 31. A method according to Claim 25 wherein each of said polyamide ligand units has three or more amide groups and two or more amine nitrogens separated by at least two carbons.

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/26435

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01D 15/00

US CL : 210/670, 679, 688; 502/401

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 210/670, 679, 681, 688; 502/401

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,078,978 A (TARBET et al) 07 January 1992, entire document.	1-3, 11-13 and 24-31
Y	US 5,096,946 A (RAINER) 17 March 1992, entire document.	1-3, 11-13 and 24-31

Further documents are listed in the continuation of Box C.

See patent family annex.

Special categories of cited documents:		"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search  
24 DECEMBER 2000

Date of mailing of the international search report

23 JAN 2001

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**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US00/26435

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.: 4-10 AND 14-23 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**  

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.